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TITLE PHOTOCHEMISTRY:PAST AND PRESENT

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## Photochemistry: Past and Present

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### Abstract

Photochemistry has been influenced greatly by the application of lasers as excitation sources. Comparisons are made below to illustrate this impact and to show how lasers have revolutionized this research field.

### Advantages of high intensity excitation sources

Prior to the utilization of ultraviolet-visible lasers in photochemistry the population of excited electronic states, the workhorses in ultraviolet-visible photochemistry, was achieved by various types of lamp sources. The intensity afforded by most conventional lamp sources is quite low and restricts the type of electronic transitions that can be studied. High-powered ultraviolet-visible lasers have permitted the photochemist to study electronically-excited states resulting via optically-forbidden transitions.

Emission studies are one of the most useful research techniques available to the photochemist. These types of studies permit the photochemist to elucidate the important dynamics and spectroscopy of his research. Fluorescence, the radiative transition between states of the same multiplicity, has been studied for decades. The conventional spectrofluorimeter depended upon a lamp to serve as the excitation source.

Phosphorescence, the radiative transition between states of unlike multiplicities, has also been studied for decades. However, phosphorescence violates spin selection rules, and consequently the emitting state, prior to laser excitation sources, had to be populated via an indirect route. For example, if the ground electronic state were a singlet, then the optical excitation route would be limited to accessing directly one of the electronically-excited singlet states. From this state nonradiative processes must occur to a triplet level (or some other nonsinglet level). After this indirect method of triplet population the excited triplet can radiate to the ground singlet and produce phosphorescence.

Lasers have afforded the photochemist several major advantages in performing emission studies. Short-pulsed lasers have made time-resolved studies, in either fluorescence or phosphorescence studies, simple to undertake. Previously, typical high-powered flashlamps had pulse durations of microseconds. Today's typical laser, used for time-resolved studies, has a pulsewidth of a few nanoseconds, and in some cases can extend to the picosecond regime. It is possible to excite forbidden transitions directly in order to study phosphorescence. Figure 1 depicts a phosphorescence excitation spectrum for the  $\text{SO}_2(^3\text{B}_1) - \text{SO}_2(\text{X } ^1\text{A}_1)$  system.<sup>1</sup> This could not have been obtained prior to the development of lasers.

### State-to-state chemistry

State-to-state chemistry was not feasible before the utilization of lasers. It was possible, of course, to use a narrow linewidth lamp to populate some species in well-defined quantum states. However, the restrictions on available candidates were enormous due to the limited choice of excitation wavelengths. With very narrow bandwidth tunable dye lasers, state-to-state chemistry is now accomplished routinely.

Let us now consider several examples of state-to-state chemistry.  $\text{SO}_2$  is a well-studied molecule which has defied a proper understanding of its spectroscopy and dynamics for a long time. One of the recent controversies involved an interpretation of the nonlinear Stein-Volmer plots that were obtained at high pressures for  $\text{SO}_2(^3\text{B}_1) - \text{SO}_2(\text{X } ^1\text{A}_1)$  phosphorescence. One of the issues that had to be considered was whether or not part of the difficulty arose because the studies had initially populated the singlet manifolds with subsequent population of the triplet state. Direct state-to-state excitation of the  $\text{SO}_2(^3\text{B}_1, 0,0,0)$  level helped clarify this issue and showed that the problem was confined to depopulation of the  $^3\text{B}_1$  state.<sup>2</sup>

State-to-state chemistry can even be performed on reactive intermediates. For example, many radicals have been produced easily in state-selective quantum levels. Much work has been done on the HS radical.<sup>3</sup>

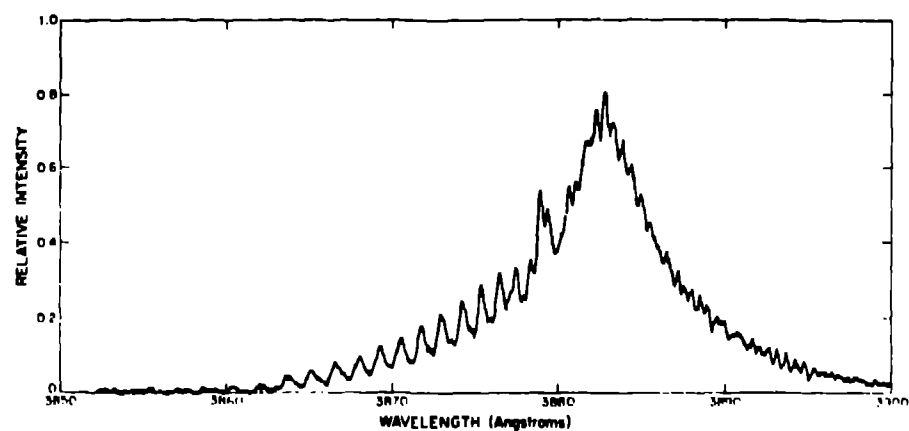


Figure 1

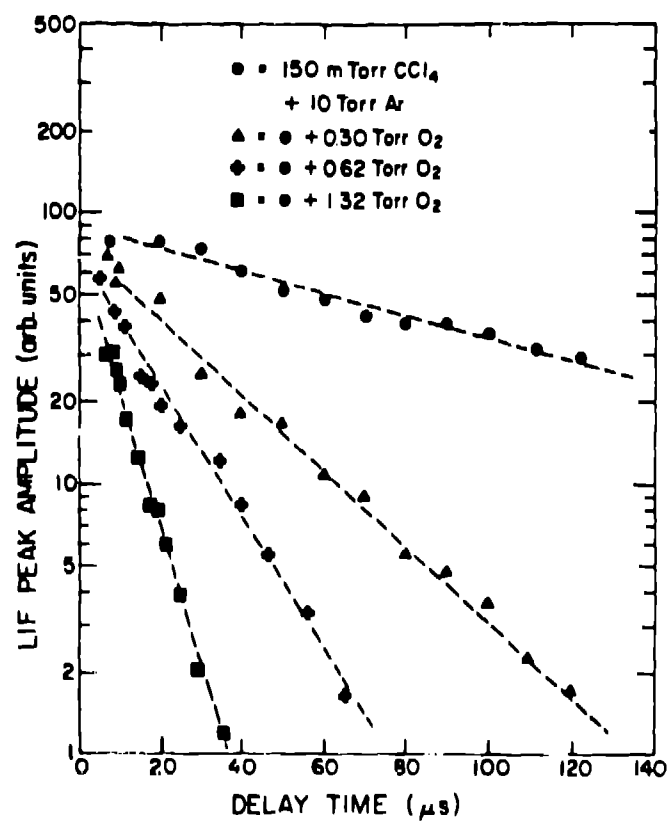


Figure 2

### Kinetic studies with lasers

The field of reaction kinetics studied via photochemical techniques has been changed drastically by modern laser technology. Absolute rate constants for radical-molecule and radical-radical reactions were previously difficult or impossible to measure because of the difficulty in measuring concentrations of radicals.

$\text{CH}_3 + \text{CH}_3$  radical combination has been studied extensively over the years. The rate constant for the reaction has been determined by several investigators. A recent study utilized a diode laser absorption technique at  $608 \text{ cm}^{-1}$  to monitor the  $\text{CH}_3$  radical concentrations that were produced by the KrF laser photolysis of  $\text{CH}_3\text{I}$ .<sup>4</sup> These lasers permitted the investigators to obtain a value for the recombination rate constant of  $(4.7 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Reactions of  $\text{CCl}$ ,  $\text{CCl}_2$ , and  $\text{CClF}$  radicals have been studied utilizing laser-induced fluorescence (LIF) to monitor radical concentrations produced by excimer laser photolysis of the appropriate precursors.<sup>5</sup> These studies would have been impossible to perform prior to the development of the appropriate excimer and dye lasers. Figure 2 displays the disappearance of  $\text{CCl}$  radicals, monitored via LIF, in the presence of varying pressures of oxygen.

### Multiple-photon photochemistry

The high intensities afforded by lasers has opened up one entirely new research area: multiple-photon photochemistry. The high intensities produced by powerful  $\text{CO}_2$  infrared lasers has made it possible to photodissociate molecules from their ground electronic state via absorption of sufficient quanta of vibrational energy. The literature has been inundated with studies of this nature since  $\text{SF}_6$  was first dissociated.<sup>6,7</sup> Infrared multiple-photon dissociation of molecules has become commonly accepted as a tool for the photochemist to generate free radicals.

Ultraviolet multiple-photon photochemistry has also come into prominence. Two of the earlier papers in this field involved the excimer laser photolysis of  $\text{CF}_2\text{Br}_2$ .<sup>8,9</sup> Many interesting results were obtained from these studies. Perhaps the most significant result is that the  $\text{CF}_2$  ( $X^1A_1$ ) radicals initially formed in the KrF laser photolysis have a resonant transition with the laser,  $\text{CF}_2(^1B_1, 060 - X^1A_1, 000)$ , producing an enormous population of the  $^1B_1$  state. This results in a very large LIF signal for the  $\text{CF}_2$  radical.

Multiple-photon photochemistry can involve simultaneously ir and uv photons. A recent study involved the ArF laser photolysis of highly vibrationally excited  $\text{SF}_6$  molecules.<sup>10</sup> In this study  $\text{SF}_6$  molecules were produced in highly vibrationally excited states by first irradiating them with a pulsed  $\text{CO}_2$  laser. Subsequently an ArF laser (193 nm) photodissociated these vibrationally excited  $\text{SF}_6$  molecules. The results indicated that the excited  $\text{SF}_6$  molecules had very different spectral features than their thermal counterparts.

### Isotope separation

Isotope separation via photochemical techniques was demonstrated prior to the application of lasers to this research area.<sup>11,12</sup> However, the restrictions using resonance lamps are overwhelming due to available candidates to match resonance lines with an appropriate isotopic shift. With tunable lasers, this is not a constraint. Laser isotope separation (LIS) has been performed using infrared, ultraviolet, and infrared plus ultraviolet lasers. Today the literature abounds with examples of LIS successes.

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